Thermodynamic Properties of Phosphorus Compounds*

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(Received June 13, 1936)

With Raman spectrum, electron diffraction and existing equilibrium data the standard virtual entropies of P(*s*, white), $P_4(g)$. $PCl_3(g)$, $PCl_3(l)$, $PCl_5(g)$, and $PCl_5(s)$ are calculated to be 10.55, 66.88, 74.7, 52.8, 87.7, and 40.8 cal./deg. respectively. The corresponding standard free energies of formation are calculated to be (0), 5850, −64,650, −63,570, −72,540 and −77,950 cal., respectively.

INTRODUCTION

THE determination of the thermodynamic properties of phosporus compounds has been prevented by the lack of a reliable value for the entropy of solid white phosphorus. Attention should be called to the fact that low temperature specific heat data for elementary phosphorus do not exist. Because of the importance of phosphorus compounds it is highly desirable to have such information. Preliminary values for the entropy of white phosphorus, 14.9 and 15.5 cal./deg., were previously obtained[1] by dubious extrapolation of not too accurate high temperature equilibrium data; though in surprisingly good agreement with each other, the values seem to be too high.

In this paper is presented what is felt to be a reasonably reliable value for the entropy of phosphorus calculated from Raman spectrum, electron diffraction, and vapor pressure data. From this result, combined with heats of formation and certain equilibrium data, are calculated the thermodynamic properties of phosphorus trichloride and phosphorus pentachloride.

CALCULATIONS

Phosphorus vapor

It is known that at room temperature solid, white phosphorus, as well as the vapor above it, consists of P_4 molecules. Electron diffraction experiments have recently shown that the structure of the P_4 molecule is that of a regular tetrahedron with a *P–P* distance of 2.21A.[2] This leads to a moment of inertia of 248×10^{-40} g, cm.[2]

The three vibrational frequencies of the P_4 molecule[3] have been found to be $\nu_1\{2\}=372(1)$, $\nu_2\{3\}=463(3)$, and $\nu_3\{1\}=607(6)$ cm^{-1}, where numbers in braces indicate the degeneracies of the respective modes of vibration, and numbers in parentheses indicate relative intensities. There should be little doubt concerning the assignment of frequencies since the ratios of the values agree with the ratios calculated by a central force treatment[4] as well as might be expected:

$$2\nu_1\{2\}=\sqrt{2}\nu_2\{3\}=\nu_3\{1\}.$$

Assuming that the molecule is a rigid, spherical top, that the vibrations are harmonic, and that interaction between vibration and rotation may be neglected, one may calculate the entropy of $P_4(g)$ by well-known methods.[5] Neglecting effects due to nuclear spin, one then gets for the virtual entropy of P_4 gas:

$$S_{298}{}^*P_4(g)=66.88 \text{ cal./deg.}$$

From the vapor pressures of solid white phosphorus as determined by Duncan and Macrae[6] we may write the equations:

$$4P(s, \text{ white})=P_4(g),$$
$$\Delta H_{298}=13{,}220 \text{ cal.}, \quad \Delta F^\circ_{298}=5{,}850 \text{ cal.}$$

The entropy of solid phosphorus

The above equations lead to the value 10.55 for the entropy of solid white phosphorus. This value should be considerably more accurate than that previously calculated. With its aid it is now possible to compute the thermodynamic

* Publication No. 551.

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properties of any phosphorus compound whose entropy and heat of formation are known.

Phosphorus trichloride

The heats of formation[7] and vaporization[8] of PCl_3 are 75,900 cal. and -7620 cal., respectively, and the free energy of vaporization is 1080 cal. at 25°C. The entropy of $PCl_3(g)$ has been calculated[1] to be 74.7 cal./deg. One may then write:

$$P(s, \text{white})+3/2Cl_2(g)=PCl_3(l),$$
$$\Delta H=-75{,}900 \text{ cal.}, \quad \Delta F^\circ_{298}=-64{,}650 \text{ cal.},$$
$$P(s, \text{white})+3/2Cl_2(g)=PCl_3(g),$$
$$\Delta H=-68{,}280 \text{ cal.}, \quad \Delta F^\circ_{298}=-63{,}570 \text{ cal.}$$

Phosphorus pentachloride

Holland[9] has made careful equilibrium measurements on the reaction $PCl_3(g)+Cl_2(g)=PCl_5(g)$ over the temperature range 440°–630° and his results have been recalculated by Nernst.[10] The vapor pressures of $PCl_5(s)$ have been carefully measured by Smith and Lombard.[11] From these results, together with those obtained above, the following thermochemical equations may be written:

$$PCl_3(g)+Cl_2(g)=PCl_5(g),$$
$$\Delta H_T=-20{,}000-3.473\,T,$$
$$\Delta F_T^\circ=-20{,}000+7.99\,T\log_{10}T+17.27\,T,$$
$$\Delta H_{298}=-21{,}040 \text{ cal.}\ \Delta F_{298}^\circ=-8970 \text{ cal.},$$

$$PCl_5(s)=PCl_5(g),$$
$$\Delta H_T=30{,}763-38.144\,T,$$
$$\Delta F_T^\circ=30{,}763+87.83\,T\log_{10}T-302.36\,T,$$
$$\Delta H_{298}=19{,}390 \text{ cal.}, \quad \Delta F_{298}^\circ=5410 \text{ cal.},$$

$$P(s, \text{white})+5/2Cl_2(g)=PCl_5(g),$$
$$\Delta H_{298}=-89{,}316 \text{ cal.}, \quad \Delta F_{298}^\circ=-72{,}540 \text{ cal.},$$

$$P(s, \text{white})+5/2Cl_2(g)=PCl_5(s),$$
$$\Delta H_{298}=-108{,}706 \text{ cal.}, \quad \Delta F_{298}^\circ=-77{,}950 \text{ cal.}$$

From its heat of solution, Thomsen[12] obtained the value $-106{,}600$ cal. for the heat of formation of $PCl_5(s)$. The agreement is satisfactory.

If we take Giauque's[13] value, 53.31 cal./deg., for the entropy of $Cl_2(g)$, there is then obtained for the standard virtual entropies of $PCl_5(s)$ and $PCl_5(g)$, 40.8 and 87.7 cal./deg., respectively. An electron diffraction determination of the structure of PCl_5 combined with Raman data would lead to an independent determination of these quantities.

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AUGUST, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

Atomic Dimensions from the Coefficients of Compressibility and Thermal Expansion

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(Received March 23, 1936)

Starting from the equation of state $p-K(V-V_0)/V_0=RT/V-V_0$, the relation $\alpha_a/\beta=R/(V-V_0)$ is derived, where V_0 is identified with the actual volume occupied by one mole of atoms or molecules. Values of the radii of atoms for different elements are calculated from this relation and compared to the values obtained from crystal analysis. Possibility of using the relation $\alpha_a/\beta=R/(V-V_0)$ to estimate molecular dimensions in the liquid state is also referred to.

THE estimation of the size of atoms or molecules from the van der Waals equation for gases

$$p+a/V^2=RT/(V-b) \qquad (1)$$

is well known. Here b represents 4 times the actual volume of the molecules in 1 mole, and may be calculated from the relation

$$b=RT_K/8P_K, \qquad (2)$$